

## AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents and Designs Acts, 1907 to 1938.

## PATENT SPECIFICATION



Application Date: Oct. 20, 1937. No. 28598/37.

" " Jan. 11, 1938. No. 902/38.

One Complete Specification Left: Sept. 28, 1938.

(Under Section 16 of the Patents and Designs Acts, 1907 to 1938.)

Specification Accepted: Feb. 8, 1939.

500,382

## PROVISIONAL SPECIFICATION

No. 28598 A.D. 1937.

### Improvements in the Manufacture and Production of Olefine Oxides

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

It has already been proposed to prepare olefine oxides by catalytic treatment of olefines with oxygen or gases containing oxygen at elevated temperature. As catalysts it has been proposed to use especially silver alloys which have been mechanically comminuted or obtained by heating organic silver compounds.

My foreign correspondents have now found that olefine oxides are obtained in better yields than hitherto by carrying out the oxidation of the olefines in the presence of silver catalysts which have been obtained by reduction by means of hydrazine of dissolved silver compounds in admixture with other metal compounds, from which the metals can be precipitated by means of hydrazine. Catalysts have proved especially suitable which contain gold or copper or both in addition to silver. The activity of the catalysts precipitated by means of hydrazine may frequently be considerably improved by subsequent etching treatment with dilute acids, as for example nitric acid.

The reaction conditions may be the same as those used in the prior known processes for the catalytic preparation of olefine oxides from olefines. The most suitable temperatures generally speaking lie between 150° and 500°, usually between 200° and 450° Centigrade. In many cases it is preferable to work under pressure, for example at 5 or 20 atmospheres or more. The oxidation of the olefines may

for example be carried out by leading a mixture of air and ethylene at above 200° Centigrade over catalysts while using an excess of air and, in order to avoid explosions, preferably with an addition of steam. A special advantage of the new process resides in the fact that even when using an excess of olefine, in particular ethylene, the olefine oxide is obtained in a good yield and a high concentration in the reaction gases. By this method of working reaction gases can be obtained which are practically free from oxygen and can be worked up without danger of explosion. The addition of steam also increases the stability of the catalysts.

The olefines are usually used in undiluted form; they may also be reacted, however, in the presence of diluent gases, as for example other hydrocarbons, such as methane. The oxidation may also be carried out by a cyclic process, by returning the unconverted ethylene to the reaction after separation of the ethylene oxide formed and the carbon dioxide formed almost exclusively as a bye-product.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight.

#### EXAMPLE 1.

For the preparation of the catalyst, 316 parts of silver nitrate and 1.4 parts of copper nitrate are dissolved in 4000 parts of water, a solution of 1 part of gold chloride in 20 parts of water is added, 190 parts of hydrazine hydrate are allowed to drop in while cooling with ice and the whole is then heated to boiling and boiled until nitrogen is no longer evolved. The whole is then allowed to cool, filtered by suction and washed out well. The resulting metal powder is stirred for some minutes at room temperature with about 4

[Price 1/-]

Price 4s 6d

BEST AVAILABLE COPY

per cent. nitric acid, filtered by suction, washed free from acid, dried and pressed into pills.

220 parts of a catalyst prepared in the said manner are charged into a porcelain tube capable of being heated electrically. Through the tube there is led each hour a mixture of 60 parts of ethylene, 35 parts of air and from 60 to 80 parts of steam at from 250° to 350° Centigrade. Thus 4.6 parts of ethylene per hour are reacted and ethylene oxide is obtained therefrom in a yield of up to 60 per cent. calculated with reference to the amount of ethylene converted. The reaction gas contains after condensation of the steam about 3 per cent. by volume of ethylene oxide and less than 1 per cent. by volume of oxygen. The

remainder consists of unconverted ethylene and small amounts of carbon dioxide. 20

#### EXAMPLE 2.

A mixture of 110 parts of air, 11 parts of ethylene and 200 parts of steam is led at from 320° to 400° Centigrade per hour over the catalyst prepared according to Example 1 in a silver tube. The reaction gas contains after separation of the steam, ethylene oxide in a concentration of up to 2.4 per cent. by volume. The yield is from 30 to 40 per cent. with reference to the ethylene converted. 25 30

Dated this 20th day of October, 1937.

J. Y. & G. W. JOHNSON,  
47, Lincoln's Inn Fields, London, W.C.2,  
Agents.

### PROVISIONAL SPECIFICATION

No. 902 A.D. 1938.

#### Improvements in the Manufacture and Production of Olefine Oxides

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft of Frankfurt-on-Main, Germany, a Joint Stock Company, organised under the Laws of Germany) to be as follows:—

A process for the manufacture and production of olefine oxides from olefines and oxygen or gases containing oxygen, if desired in the presence of steam, is described in the specification No. 28598 A.D. 1937 according to which catalysts are used which have been obtained by the reduction of dissolved silver compounds with hydrazine in the presence of other metal compounds. 75 80

My foreign correspondents have now found that olefines can also be oxidised catalytically in good yields to form olefine oxides by using silver catalysts which have been obtained by treating solutions or suspensions of silver compounds in the presence of other metal compounds capable of being precipitated by reducing agents with reducing agents other than hydrazine or by treating suspensions of silver compounds by means of hydrazine in the presence of other metal compounds. 85 90

For the preparation of the catalysts, the initial materials are silver and other metal compounds which are either wholly or partly in true or colloidal dissolution in a liquid or are present completely as a suspension. For example it is advantageous first to dissolve the metals in the form of suitable compounds in water, to

add a precipitant to these solutions and to treat the resulting suspension with a reducing agent. Among suitable reducing agents there may be mentioned for example formaldehyde, glucose, hydroxylamine, phenyl hydrazine and other compounds which are capable at least of converting the silver compounds to metallic silver and of precipitating or reducing the other metal compounds. The catalysts thus obtained are advantageously superficially etched by treatment with dilute nitric acid dried and shaped, as for example pressed into pills, for the purpose of better handling. 95

If mixtures of olefines with oxygen or gases containing oxygen be led over such catalysts, for example under the conditions described in the said specification No. 28598 A.D. 1937, gas mixtures are obtained which contain olefine oxides in a high concentration in addition to very small amounts of oxygen. In addition to unchanged olefines and olefine oxides, the final gases usually only contain carbon dioxide and, when using air, nitrogen. By reason of the high concentration of the olefine oxides, they may be separated very readily. Furthermore the explosiveness of the final gas mixture is greatly reduced and frequently even completely removed by low oxygen concentration and the presence of carbon dioxide and any inert gases added as diluents. 100 105

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight. 110

#### EXAMPLE 1.

A solution of 1.5 parts of gold chloride

in 100 parts of water and then a solution of 329 parts of potassium hydroxide in 329 parts of water are added to a solution of 474 parts of silver nitrate and 2.1 parts of copper nitrate in 6000 parts of water. 275 parts of a 30 per cent. solution of formaldehyde are allowed to flow slowly into the mixture. The dark oxide precipitate first formed becomes pale after a short time. The mixture is heated to boiling, boiled for an hour, allowed to cool, filtered by suction and the filter residue freed from alkali and formaldehyde by washing. The powder thus obtained is treated for a short time with about 4 per cent. nitric acid, washed free from acid, dried and pressed into pills.

200 parts of the catalyst thus prepared are introduced into a silver tube through which a mixture of 20 parts of ethylene, 92 parts of air and 200 parts of steam is then led per hour at from 250° to 350° Centigrade. The gas mixture formed is almost free from oxygen and contains up to 5 per cent. of ethylene oxide in addition to a small amount of carbon dioxide. The catalyst need not be exchanged until after use for a very long time.

#### EXAMPLE 2.

A mixture of silver nitrate, copper nitrate and gold chloride solutions prepared as described in Example 1 is precipitated with potassium hydroxide solution as therein described. A solution of 60 parts of glucose in 240 parts of water is then added and the mixture slowly heated to from 70° to 80° Centigrade. After an hour the whole is allowed to cool, filtered by suction, washed out well and the mass treated for some minutes with 4 per cent. nitric acid, again washed, dried and pressed into pills.

A mixture of ethylene, air and steam in the ratio 1:10:30 is led at from 250° to 350° Centigrade in a silver tube over the catalyst prepared in the said manner. the speed of flow being equal to 128 times the volume of the catalyst per minute. A gas mixture is formed containing ethylene oxide in high concentration. The catalyst used in this case is also distinguished by a specially durable and uniform activity.

Dated this 11th day of January, 1938.

J. Y. & G. W. JOHNSON,  
47, Lincoln's Inn Fields, London. W.C.2.  
Agents.

### COMPLETE SPECIFICATION

#### Improvements in the Manufacture and Production of Olefine Oxides

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfurt-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) and in what manner the same is to be performed to be particularly described and ascertained in and by the following statement:—

It has already been proposed to prepare olefine oxides by catalytic treatment of olefines, in particular low molecular olefines such as ethylene and propylene with oxygen or gases containing oxygen at elevated temperature. As catalysts it has been proposed to use especially silver alloys which have been mechanically comminuted or obtained by heating mixtures of organic compounds of silver and the desired other metal, or metals.

My foreign correspondents have now found that olefine oxides are obtained in better yields than hitherto by carrying out the oxidation of the olefines, in particular of low molecular olefines in the presence of silver catalysts which have been obtained by reduction of solutions or suspensions of silver compounds, in other words silver

compounds in the liquid phase, by means of reducing agents. The silver compounds may also be reduced in the presence of other metal compounds, especially compounds of such metals which are capable of being precipitated and, as may be the case, reduced by the reducing agents. Catalysts have proved especially suitable which contain gold or copper or both in addition to silver. The activity of the silver catalysts obtained with the aid of reducing agents may frequently be improved by subsequent etching treatment with dilute acids, as for example nitric acid.

For the preparation of the catalysts, the initial materials are silver, and, if desired, other metal compounds which are either wholly or partly in true or colloidal dissolution in a liquid or are present completely as a suspension. For example it is advantageous first to dissolve the silver and, if desired, the other metals in the form of suitable compounds in water, to add a precipitant to these solutions and to treat the resulting suspension with a reducing agent. Among suitable reducing agents there may be mentioned for example hydrazine, formaldehyde, glucose, hydroxylamine, phenyl hydrazine and other compounds which are capable at least of converting the silver compounds

into metallic silver. They should also be capable of precipitating or reducing the other metal compounds, because otherwise these metals would not be present in the precipitated silver catalyst. The catalysts thus obtained are, if desired, superficially etched by treatment with dilute nitric acid, dried and shaped, as for example pressed in pills, for the purpose of better handling.

The reaction conditions may be the same as those used in the prior known processes for the catalytic preparation of olefine oxides from olefines. The most suitable temperatures generally speaking lie between 150° and 500°, usually between 200° and 450° Centigrade. In some cases it is preferable to work under pressure, for example at 5 or 20 atmospheres or more. The oxidation of the olefines may for example be carried out by leading a mixture of air and ethylene at above 200° Centigrade over catalysts while using an excess of air, and in order to avoid explosions, preferably with an addition of steam. A special advantage of the new process resides in the fact that even when using an excess of olefine, in particular ethylene, the olefine oxide is obtained in a good yield and a high concentration in the reaction gases. By this method of working reaction gases can be obtained which are practically free from oxygen and can be worked up without danger of explosion. The addition of steam also increases the stability of the catalysts.

The olefines are usually used in undiluted form; they may also be reacted, however, in the presence of diluent gases, as for example other hydrocarbons, such as methane. The oxidation may also be carried out by a cyclic process, by returning the unconverted ethylene to the reaction after separation of the ethylene oxide formed and the carbon dioxide formed almost exclusively as a bye-product.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight, unless otherwise stated.

#### EXAMPLE 1.

For the preparation of the catalyst, an aqueous solution of 472 parts of silver nitrate and an aqueous solution of 200 parts of potassium carbonate are mixed, while stirring, at from 20° to 25° Centigrade. The precipitate obtained is then reduced by the addition of 87.2 parts of potassium hydroxide and 46.5 parts of formaldehyde both of which are dissolved in 400 parts of water. The silver powder is filtered off by suction, washed with distilled water, dried and pressed into pills.

270 parts of a catalyst prepared in the said manner are charged into a porcelain tube capable of being heated electrically. Through the tube there is led each hour a mixture of 200 parts of air and 5 parts of ethylene at from 240° to 260° Centigrade. The reaction gas contains in addition to air about 1.2 per cent. by volume of ethylene oxide, small amounts of carbon dioxide and unchanged ethylene. The yield is up to 75 per cent. with reference to the ethylene converted.

If a mixture of 62.5 parts of ethylene, 80 parts of steam and from 10 to 20 parts of air be led over the same catalyst at from 210° to 240° Centigrade, good yields of ethylene oxide are also obtained.

#### EXAMPLE 2.

For the preparation of the catalyst a solution of 730 parts of potassium hydroxide in 6000 parts of water is allowed to flow into a solution of 474 parts of silver nitrate in 6000 parts of water, while cooling with ice. After the precipitation of the silver oxide is completed, 250 parts of a 30 per cent aqueous formaldehyde solution are added. The mixture is allowed to stand for half an hour and then heated to boiling for a further hour. While carrying out these steps, the reaction mixture is continuously stirred. The silver is filtered off by suction, washed until neutral, treated with 2 per cent nitric acid for a short time, filtered off again, washed until neutral and free from nitrate ions, dried and pressed into pills.

1350 parts by volume (0° C./760 mm.) of a mixture consisting of 58 parts of ethylene, 20 parts of air and 80 parts of steam are led each hour over 1 part by volume of the catalyst at from 240° to 250° Centigrade. A reaction gas is obtained which contains from 2 to 25 per cent by volume of ethylene oxide which corresponds to a yield of from 60 to 70 per cent with reference to the ethylene converted.

#### EXAMPLE 3.

570 parts of hydrazine hydrate are allowed to flow into a solution, cooled at 0° Centigrade, of 948 parts of silver nitrate in 12000 parts of water, while stirring. After having stirred the suspension formed for one hour, it is filtered off, washed until neutral, treated with 2 per cent nitric acid for some minutes, again filtered off, washed and finally dried and pressed into pills. A mixture of ethylene, air and steam is led over the catalyst as described in Example 2, about the same yields of ethylene oxide being obtained.

#### EXAMPLE 4.

For the preparation of the catalyst, 316 parts of silver nitrate and 1.4 parts of

copper nitrate are dissolved in 4000 parts of water, a solution of 1 part of gold chloride in 20 parts of water is added, 190 parts of hydrazine hydrate are allowed to drop in while cooling with ice and the whole is then heated to boiling and boiled until nitrogen is no longer evolved. The whole is then allowed to cool, filtered by suction and washed out well. The resulting metal powder is stirred for some minutes at room temperature with about 4 per cent nitric acid, filtered by suction, washed free from acid, dried and pressed into pills.

220 parts of a catalyst prepared in the said manner are charged into a porcelain tube capable of being heated electrically. Through the tube is led each hour a mixture of 60 parts of ethylene, 35 parts of air and from 60 to 80 parts of steam at from 250° to 350° Centigrade. Thus 4.6 parts of ethylene per hour are reacted and ethylene oxide is obtained therefrom in a yield of up to 60 per cent calculated with reference to the amount of ethylene converted. The reaction gas contains after condensation of the steam about 3 per cent by volume of ethylene oxide and less than 1 per cent by volume of oxygen. The remainder consists of unconverted ethylene and small amounts of carbon dioxide.

#### EXAMPLE 5.

A mixture of 110 parts of air, 11 parts of ethylene and 200 parts of steam is led at from 320° to 400° Centigrade per hour over the catalyst prepared according to Example 4 in a silver tube. The reaction gas contains, after separation of the steam, ethylene oxide in a concentration of up to 2.4 per cent by volume. The yield is from 30 to 40 per cent with reference to the ethylene converted.

#### EXAMPLE 6.

A solution of 1.5 parts of gold chloride in 100 parts of water and then a solution of 329 parts of potassium hydroxide in 329 parts of water are added to a solution of 474 parts of silver nitrate and 2.1 parts of copper nitrate in 6000 parts of water. 275 parts of a 30 per cent solution of formaldehyde are allowed to flow slowly into the mixture. The dark oxide precipitate first formed becomes pale after a short time. The mixture is heated to boiling, boiled for an hour, allowed to cool, filtered by suction and the filter residue freed from alkali and formaldehyde by washing. The powder thus obtained is treated for a short time with about 4 per cent nitric acid, washed free from acid, dried and pressed into pills.

200 parts of the catalyst thus prepared are introduced into a silver tube through which a mixture of 20 parts of ethylene, 92 parts of air and 200 parts of steam is

then led per hour at from 250° to 350° Centigrade. The gas mixture formed contains up to 3 per cent of ethylene oxide in addition to carbon dioxide. The catalyst need not be exchanged until after use for a very long time.

#### EXAMPLE 7.

A mixture of silver nitrate, copper nitrate and gold chloride solution prepared as described in Example 6 is precipitated with potassium hydroxide solution as therein described. A solution of 60 parts of glucose in 240 parts of water is then added and the mixture slowly heated to from 70° to 80° Centigrade. After an hour the whole is allowed to cool, filtered by suction, washed out well and the mass treated for some minutes with 4 per cent nitric acid, again washed, dried and pressed into pills.

A mixture of ethylene, air and steam in the ratio 1:10:30 is led at from 250° to 350° Centigrade in a silver tube over the catalyst prepared in the said manner, the speed of flow being equal to 128 times the volume of the catalyst per minute. A gas mixture is formed containing ethylene oxide in high concentration. The catalyst used in this case is also distinguished by a specially durable and uniform activity.

I am aware of Specification No. 501,278 wherein a process for the catalytic oxidation or hydrogenation of ethylene is described and claimed according to which silver catalysts are employed which have been obtained by subjecting silver or silver compounds in an aqueous medium to the action of hydrogen *in statu nascendi*. I do not claim the oxidation of ethylene as claimed and described in Specification No. 501,278.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that subject to the foregoing disclaimer what I claim is:—

1. A process for the manufacture and production of olefine oxides by catalytic oxidation of low molecular olefines with oxygen or gases containing oxygen, which consists in carrying out the oxidation in the presence of silver catalysts which have been prepared by reduction of solutions or suspensions of silver compounds by means of reducing agents.

2. A modification of the process as claimed in claim 1 which consists in reducing the silver compounds in the presence of copper or gold compounds.

3. A modification of the process as claimed in claim 1 or 2, which consists in superficially etching the silver catalysts by treatment with dilute nitric acid.

4. The process for the manufacture and production of olefine oxides substantially

as described in each of the foregoing  
Examples.

5. Olefine oxides when prepared in  
accordance with the process particu-  
larly described and ascertained or its  
obvious chemical equivalents.

Dated this 28th day of September, 1938.

J. Y. & G. W. JOHNSON,  
47, Lincoln's Inn Fields,  
London, W.C.2,  
Agents.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1939.

BEST AVAILABLE COPY